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# D E C L A R A T I O N

In the matter of U.S. Patent Application Ser. No. 09/914,482 in the name of Masahiro YATAKE

I, KONNO Akio, of Kyowa Patent and Law Office, 2-3, Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, declare and say:

that I am thoroughly conversant with both the Japanese and English languages; and,

that the attached document represents a true English translation of Japanese Patent Application No. 1999-375315 filed on December 28, 1999.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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[TITLE OF DOCUMENT] SPECIFICATION 11-375315

[TITLE OF INVENTION] INK SET FOR INK JET RECORDING AND AN INK JET RECORDING APPARATUS

[SCOPE OF CLAIMS]

[Claim 1]

An ink set for ink jet recording:

wherein an ink-jet recording ink used for an ink jet recording apparatus using at least two or more inks comprises a compound represented by the following formula (I):

[Chemical formula 1]

formula (I):

$$G1-(EP)_n$$

wherein

G1 represents a glycerin structure;

EP represents an ethyleneoxy and/or propyleneoxy group, optionally, an OH group; and

n represents an average of addition units, ranging from 0.5 to 10; and

wherein the difference in viscosity between said two or more inks at 15°C to 45°C falls within 5%.

[Claim 2]

The ink set for ink jet recording according to claim 1, wherein said ink-jet recording ink has a surface tension of not more than 40 mN/m.

[Claim 3]

The ink set for ink jet recording according to claim 1, wherein said ink-jet recording ink used for the ink set for ink jet recording comprises glycerin and the compound represented by formula (I), and wherein the difference in viscosity between said two or more inks at from 15°C to 45°C falls within 5%.

[Claim 4]

The ink set for ink jet recording according to claim 1,

wherein said ink-jet recording ink for the ink jet recording apparatus using at least two or more inks comprises the compound represented by the following formula (I), wherein the difference in viscosity between the two or more inks at 15°C to 45°C falls within 5%, and wherein said at least two or more inks are identical to each other in color.

[Claim 5]

The ink set for ink jet recording according to claim 1, wherein, when a coloring agent contained in each of the inks used for said ink set for ink jet recording is a pigment, as measured at 15°C to 45°C with a rotating viscometer at a torque of 1 mN·m to 100 N·m, the change in viscosity of each ink is not more than 5%.

[Claim 6]

The ink set for ink jet recording according to claim 1, wherein the amount of a colorant contained in at least one ink among said at least two or more inks used for said ink set for ink jet recording is more than 5% by weight.

[Claim 7]

The ink set for ink jet recording according to claim 1, wherein n in the formula (I) ranges from 0.5 to 10.

[Claim 8]

The ink set for ink jet recording according to claim 1, wherein a repeating unit (EP) multiplied by n in the formula (I) is an ethyleneoxy and/or propyleneoxy group, and wherein the compound of the formula (I) has a molecular weight distribution in the ink-jet recording ink.

[Claim 9]

The ink set for ink jet recording according to claim 1, wherein the compound represented by the formula (I) has an average molecular weight of 1,000 or less.

[Claim 10]

The ink set for ink jet recording according to claim 2, wherein said ink-jet recording ink used for the ink set for ink jet recording has a surface tension of not more than 40 mN/m and comprises a 1,2-alkylene glycol which may be branched, wherein the proportion of the 1,2-alkylene glycol which may be branched to the compound represented by the formula (I) is 2 or more with the proviso that the amount of the 1,2-alkylene glycol which may be branched is not less than 3% by weight, wherein the 1,2-alkylene glycol which may be branched and which has 4 to 10 carbon atoms is 1,2-pentanediol which may be branched and/or 1,2-hexanediol which may be branched, and wherein the amount of the 1,2-pentanediol which may be branched ranges from 0.5% to 20% by weight and the amount of the 1,2-hexanediol which may be branched 0.3 to 15.

[Claim 11]

The ink set for ink jet recording according to claim 2, wherein said ink-jet recording ink used for the ink set for ink jet recording has a surface tension of not more than 40 mN/m and comprises 0% to 10% by weight of (di)propylene glycol monobutyl ether, and wherein the ratio between the (di)propylene glycol monobutyl ether and the 1,2-alkylene glycol which may be branched and which has 4 to 10 carbon atoms ranges from 1 : 0 to 1 : 10.

[Claim 12]

The ink set for ink jet recording according to claim 2, wherein said ink-jet recording ink used for the ink set for ink jet recording has a surface tension of not more than 40 mN/m and comprises 0% to 5% by weight of an acetylene glycol surfactant, and wherein the ratio between the acetylene glycol surfactant and the 1,2-alkylene glycol which may be branched and which has 4 to 10 carbon atoms ranges from 1 : 0 to 1 : 3.

[Claim 13]

The ink set for ink jet recording according to claim 1, wherein said ink-jet recording ink used for the ink set for ink jet recording has a surface tension of not more than 40 mN/m and comprises 0% to 20% by weight of di(tri)ethylene glycol monobutyl ether, and wherein the ratio between the di(tri)ethylene glycol monobutyl ether and the 1,2-alkylene glycol which may be branched and which has 4 to 10 carbon atoms ranges from 1 : 0 to 1 : 10.

[Claim 14]

The ink-jet recording ink according to claim 1, wherein a colorant contained in said ink-jet recording ink comprises a water-soluble dye and/or a water-soluble pigment which is dispersible in water.

[Claim 15]

The ink set for ink jet recording according to claim 1, wherein the pigment used for said ink-jet recording ink is dispersible in water by surface oxidization.

[Claim 16]

An ink jet recording apparatus using said ink set for ink jet recording.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical field]

The present invention relates to an ink-jet recording ink which can offer excellent print quality to plain papers, recycled papers or coated papers.

[0002]

[Prior art]

An ink jet recording method is a printing method wherein droplets of an ink are ejected and scattered, and are deposited onto recording media to print letters or figures. Examples of

ink jet recording methods which have been put to practical use include: a method wherein an electric signal is converted to a mechanical signal using an electrostrictive element to intermittently eject an ink reservoired in a nozzle head section, thereby recording letters or symbols on the surface of a recording medium; and a method wherein an ink, reservoired in a nozzle head section, in its portion very close to the ejection portion is rapidly heated to create a bubble and the ink is intermittently ejected by volume expansion created by the bubble to record letters or symbols on the surface of a recording medium.

[0003]

Various properties required of inks used in the above ink jet recording are such that the drying property of the print is good, no significant feathering is created in printed images, uniform printing can be realized on the surface of conventional recording media, and, in the case of multi-color printing, mixing between adjacent colors does not occur. Further, what is important to inks is to ensure satisfactory ejection stability of ink at actual service temperatures of ink jet recording apparatuses.

[0004]

Therefore, various studies have hitherto been made on components in inks. Accordingly, various solvents as additives have been examined. For example, as disclosed in U.S. Patent No. 5,156,675, the use of diethylene glycol monobutyl ether has been proposed for reducing feathering or bleeding by lowering the surface tension of an ink and increasing the penetration speed of the ink composition into paper. The use of Surfynol 465 (manufactured by Air Products and Chemicals Inc., U.S.A.) as an acetylene glycol surfactant as disclosed in U.S. Patent No. 5,183,502, or the combined use of diethylene glycol

monobutyl ether and Surfynol 465 as disclosed in U.S. Patent No. 5,196,056, has been proposed. Further, an ink has been proposed which contains, as a wetting agent, polyglycerin as disclosed in Japanese Patent Laid-Open Publication No. 152170/1991, polyglycerin with an ethyleneoxy group added thereto as disclosed in Japanese Patent Laid-Open Publication No. 328644/1997, or glycerin with an ethyleneoxy group added thereto in order that the ink may not dry on the front face of the nozzle in the recording head when the ink is not ejected for a long period of time as disclosed in Japanese Patent Laid-Open Publication No. 18465/1992. However, examples wherein an electrostrictive element is used are specifically not disclosed. Further, a recording head using an electrostrictive element has a great advantage such that the head can eject ink droplets several hundred millions of times since the recording head can be used without thermal damage to the ink. It is possible to make long and large printings since the recording head can be used as a permanent head. Further, Japanese Patent Laid-Open Publication No. 157698/1995 discloses examples of an ink using a 1,2-alkylene glycol to reduce bleeding of the dye. This publication, however, does not disclose pigment-based inks. Unlike dyes, pigments are advantageously superior in waterfastness, lightfastness, and weatherfastness.

[0005]

Although various studies have been made on additives other than those stated above, there are no specific disclosures that a moisturizing agent and a penetrant are used in combination and that the ejection stability of an ink-jet ink is ensured.

[0006]

[Problem to be solved by the invention]

For these conventional inks, however, there is still room for improvement. Specifically in the case of printing on plain paper, for example, mere addition of an adduct of ethyleneoxy groups with glycerin to inks sometimes causes prolongation of drying time due to high surface tension. Therefore, when printing is continuously carried out on a plurality of sheets, there is fear that satisfactory drying time cannot be ensured and, thus, immediately after printing, prints cannot be put on top of one another. This is disadvantageous in high-speed printing. However, there are no specific disclosures as to examples using an electrostrictive element. In examples of inks using a 1,2-alkylene glycol, while the reduction of dye color mixing is described, there is no disclosure of pigment-based inks. In general, pigments are less likely to cause color mixing, and thus this concept does not apply to pigments. Further, mere use of the 1,2-alkylene glycol is likely to cause clogging, particularly when used in a head using an electrostrictive element.

[0007]

The present invention can provide an ink set for ink jet recording wherein an ink-jet recording ink comprises at least a colorant and water and has a surface tension of not more than 40 mN/m, and wherein the difference in viscosity between two or more inks at from 15°C to 45°C falls within 5% by controlling the amount of the compound represented by formula (I), whereby the print quality can be improved much more than those in conventional art. In particular, even when heads using an electrostrictive element are used, there is provided the ink set for ink jet recording which can offer improved ejection stability.

[0008]

Accordingly, the present invention has been made for

solving the above problems, and an object of the present invention is to provide an ink set for ink jet recording having excellent ejection stability, particularly in a head using an electrostrictive element.

[0009]

[Means for solving the problem]

An ink set for ink jet recording according to the present invention is characterized in that the difference in viscosity between two or more inks at 15°C to 45°C is controlled to fall within 5% by the amount of a compound represented by the following formula (I) as a component of an ink-jet recording ink used for an ink jet recording apparatus using at least the two or more inks.

[0010]

[Chemical formula 2]

formula (I):

$$G1-(EP)_n$$

wherein

G1 represents a glycerin structure;

EP represents an ethyleneoxy and/or propyleneoxy group, optionally, an OH group; and

n represents an average of addition units, ranging from 0.5 to 10.

[0011]

[Embodiments of the Invention]

In the present invention, extensive research has been made on a composition so that an ink set for ink jet recording can provide improved stability of ink ejection.

[0012]

An ink set for ink jet recording according to the present invention is characterized in that the difference in viscosity between at least two or more inks at 15°C to 45°C falls within

5% by regulating the amount of a compound represented by the following formula (I) as a component of an ink-jet recording ink used for an ink jet recording apparatus using the at least two or more inks.

[0013]

[Chemical formula 3]

formula (I):

$$G1-(EP)_n$$

wherein

G1 represents a glycerin structure;

EP represents an ethyleneoxy and/or propyleneoxy group, optionally, an OH group; and

n represents an average of addition units, ranging from 0.5 to 10.

[0014]

In the present invention, 15°C to 45°C refer to actual service temperatures of the inks in printers, and the difference in viscosity in the above temperature range falls within 5%, whereby the frequency dependency of ink ejection is good and printing can be stably carried out. It becomes easy to control the viscosity without affecting frequency characteristics and the like by regulating the amount of the compound represented by formula (I). In general, when the inks are different from each other or one another in dyes and pigments, the molecular weight and the particle diameter vary from ink to ink. Therefore, the viscosity of the ink set is controlled by the addition of additives. When inks different from each other in molecular weight or polarity of materials are used, the inks are different from each other in frequency characteristics of ink ejection, and consequently the control thereof is likely to be difficult.

[0015]

The ink-jet recording ink for the ink set for ink jet recording according to the present invention is characterized in that the ink-jet recording ink has the surface tension of not more than 40 mN/m. When the surface tension exceeds 40 mN/m, the ink does not easily penetrate ordinary paper, such as plain paper, and it takes long for the ink to dry. Therefore, there is a problem that in continuous printing, traces of previous print are left on paper which has been placed on the previous prints (called offset phenomenon), so that high-speed printing is impossible.

[0016]

Further, the ink-jet recording ink for the ink set for ink jet recording is characterized in that, when glycerin is used in the ink-jet recording ink for the ink set, the difference in viscosity between the two or more inks at 15°C to 45°C is controlled to fall within 5% based on the total amounts of glycerin and a compound represented by the following formula (I). This is because glycerin and the compound represented by formula (I) can be uniformly mixed together in any amounts and, in addition, glycerin and the compound represented by formula (I) are less likely to affect frequency characteristics of inks while, considering that the compound represented by formula (I) also contains glycerin, it is reasonable to examine the mixing proportion of the compound represented by formula (I) to glycerin.

[0017]

The ink for jet recording in the ink set for ink jet recording apparatus using at least two or more inks is characterized in that, when the difference in viscosity between the two or more inks at 15°C to 45°C is controlled to fall within 5% by regulating the amount of the compound represented by formula (I). In particular, in ink-jet recording ink, there

is a case where a shading difference in similar color inks is made by varying the amount of a colorant to be added. In this case, when the viscosity difference is made merely by adding glycerin, feathering or bleeding increases due to a large quantity of glycerin contained in one ink. However, the degree of feathering or bleeding is less likely to be different by regulating the viscosity by a compound represented by formula (I). Examples of similar colors include the case where a magenta ink and a magenta ink having low color density (light magenta) are combined, for example, black, cyan, yellow, orange, or green ink is combined with the respective ink having low color density (light color ink).

[0018]

The individual ink for the ink set for ink jet recording is characterized in that the change in viscosity of each ink is controlled to fall within 5% by regulating the torque of the rotating viscometer within the above range, thereby grasping the pseudoplastic flow properties of each ink. Therefore, a difference in frequency characteristics between inks in ink jet recording can be minimized.

[0019]

The ink set for ink jet recording is characterized in that the amount of a colorant contained in at least one ink of two or more inks used for the ink set exceeds 5% by weight. When the difference in viscosity between the inks is controlled to fall within 5%, an ink containing a large amount of solid matter has a problem that the printing stability is not good and that the frequency characteristics are different. Particularly, when the amount of a colorant is more than 5% by weight, the problem occurs. Since a colorant in an amount of 5% by weight is difficult to appear in color density, it is common that an ink for jet recording at a minimum contains at least 5% or more

by weight of colorant.

[0020]

It is characterized that n in the aforesaid formula (I) ranges from 0.5 to 10. n represents the number of an ethyleneoxy group and/or a propyleneoxy group and is preferably 0.5 or more on average. When n is 0.5 or less, the improvement on the print quality decreases. Reversely, when n is 10 or more, the viscosity increases, so that the ink becomes difficult to be used. Therefore, a preferred value is 2 to 8, a more preferred value is 3 to 6. Processes usable for the production of the compound represented by formula (I) include, for example, a production process wherein glycerin is used as a starting compound and target molar amounts of ethylene oxide and propylene oxide are added to glycerin in an atmosphere of an alkali or the like, and a production process wherein a glycol compound, such as ethylene glycol, diethylene glycol, or propylene glycol, is added with dehydration to glycerin. In general, the compound represented by formula (I) is unlikely to be a single compound while the compound may be used as a single compound through a conventional process, such as distillation. From the viewpoint of the anticlogging property and improved print quality, however, it is preferred that a repeating unit (EP) multiplied by n in the formula (I) is an ethyleneoxy and/or propyleneoxy group, the compound of the formula (I) has a molecular weight distribution in the inks for ink jet recording system when the ink is used in a head using an electrostrictive element as in the present invention. Note that a method wherein an ejection portion is rapidly heated to create a bubble for printing is not necessarily eliminated and has the similar advantages.

[0021]

It is characterized that the compound represented by

formula (I) has an average molecular weight of not more than 1000. When the average molecular weight exceeds 1000, the viscosity increases, so that the compound becomes difficult to be used. Consequently, the improvement of the print quality is hardly produced. The average molecular weight is more preferably not more than 800, still more preferably not more than 600.

[0022]

It is characterized in that the ink used for the ink set for ink jet recording comprises a 1,2-alkylene glycol which may be branched as a compound for controlling the surface tension of the ink to be within not more than 40 mN/m, that the proportion of the 1,2-alkylene glycol which may be branched to the compound represented by the formula (I) is 2 or more when the content of the 1,2-alkylene glycol which may be branched is not less than 3% by weight, and that the 1,2-alkylene glycol which may be branched and which has 4 to 10 carbon atoms is 1,2-pentanediol and/or 1,2-hexanediol which may be branched. Further, it is preferred that the amount of the 1,2-pentanediol which may be branched ranges from 0.5% to 20% by weight and the amount of the 1,2-hexanediol which may be branched is 0.3 to 15.

[0023]

It is characterized in that the ink used for the ink set for ink jet recording comprises 0% to 10% by weight of (di)propylene glycol monobutyl ether to control the surface tension of the ink to fall within not more than 40 mN/m. It is preferred that the ratio between the (di)propylene glycol monobutyl ether and the 1,2-alkylene glycol which may be branched and which has 4 to 10 carbon atoms ranges from 1 : 0 to 1 : 10. The ink-jet recording ink according to the present invention has an improved penetration property, and (di)propylene glycol monobutyl ether is exemplified as one

improving penetration property. The amount of (di)propylene glycol monobutyl ether added is preferably 0% to 10% by weight for reaching a suitable penetration level. When the amount thereof exceeds 10% by weight, the water solubility of the ink is lowered, and consequently the ink is unsuitable for the water-soluble ink jet recording system. The amount thereof is more preferably 0.5% to 5% by weight.

[0024]

It is characterized in that the ink used for the ink set for ink jet recording comprises 0% to 5% by weight of an acetylene glycol surfactant to control the surface tension of the ink to fall within not more than 40 mN/m and that the ratio between the acetylene glycol surfactant and the 1,2-alkylene glycol which may be branched and which has 4 to 10 carbon atoms ranges from 1 : 0 to 1 : 3. The addition of acetylene glycol surfactant can further improve print quality. The amount of the acetylene glycol surfactant added is 0% to 5% by weight. The addition of more than 5% by weight of the acetylene glycol surfactant does not improve print quality, reversely causing a problem of viscosity increase. The amount of the acetylene glycol surfactant added is more preferably 0.1% to 2% by weight. Further, it is characterized in that the ratio between the compound represented by the aforesaid formula (I) and the acetylene glycol surfactant ranges from 1 : 0 to 1 : 3. Acetylene glycol surfactants usable in the present invention include, for example, Surfynol series manufactured by Air Products and Chemicals Inc. The ratio of the acetylene glycol surfactant to the compound of formula (I) is preferably in the range of 1 : 0 to 1 : 3, i.e., the amount of the acetylene glycol surfactant preferably ranges from 0% by weight to the amount three times as much as that of the compound of formula (I). The preferred amount of the compound of formula (I) ranges from 0.5%

to 30% by weight. When the amount of the compound of formula (I) is 0.5% by weight at minimum rate, the amount of the acetylene glycol surfactant is 1.5% by weight. If an amount exceeding 1.5% by weight is added, the effect obtained by the addition decreases and the print quality improvement is not made, and thus the amount to the above level is preferred.

[0025]

It is characterized in that the ink used for the ink set for ink jet recording comprises 0% to 20% by weight of di(tri)ethylene glycol monobutyl ether as a compound for controlling the surface tension of the ink to fall within not more than 40 mN/m, and that the ratio between the di(tri)ethylene glycol monobutyl ether and the 1,2-alkylene glycol which may be branched and which has 4 to 10 carbon atoms ranges from 1 : 0 to 1 : 10. From the viewpoint of the improvement of the printing quality and the water solubility, the addition of di(tri)ethylene glycol monobutyl ether is preferred. The amount thereof is controlled to be from 0% to 20 % by weight.

[0026]

The aforesaid colorants for the ink-jet recording ink are suitable for water-soluble dyes and/or water-soluble pigments which are dispersible in water. Further, it is preferred that pigments usable for the ink-jet recording ink can be dispersible in water by surface oxidation. Examples of the water-soluble dyes used herein include acid dyes, basic dyes, direct dyes and disperse dyes. The surface treated pigment is also stable against glycol ethers, for example, (di)propylene glycol monobutyl ether and di(tri)ethylene glycol monobutyl ether which are preferably used herein. This is advantageous over the dispersion of the pigment with the aid of a dispersant in that the ink-jet recording ink can withstand severer conditions

and, at the same time, can be stably used even under high-temperature or low-temperature conditions.

[0027]

An ink jet system capable of providing stable ejection can be realized by the ink jet recording apparatus using the above ink set for ink jet recording.

[0028]

Further, the ink-jet recording ink according to the present invention may properly contain optional ingredients, such as preservatives, antioxidants, electric conductivity adjustors, pH adjustors, viscosity modifiers, other surface tension modifiers, and oxygen absorbers.

[0029]

Water-soluble glycols are preferably used for preventing the ink from being dried mainly at the front face of nozzles in the recording head. Examples of water-soluble glycols usable herein include ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, polyethylene glycol having a molecular weight of not more than 2000, 1,3-propylene glycol, isopropylene glycol, isobutylene glycol, 1,4-butanediol, 1,3-butanediol, 1,2-pentanediol, 1,5-pentanediol, 1,2-hexanediol, 1,6-hexanediol, 1,2,6-hexanetriol, 1,8-octanediol, 1,2-octanediol, glycerin, mesoerythritol, and pentaerythritol.

[0030]

Saccharides may be used as nozzle clogging preventives for preventing the ink from being dried at the front face of nozzles in the recording head. Saccharides include monosaccharides and polysaccharides. More specific examples usable herein include glucose, mannose, fructose, ribose, xylose, arabinose, lactose, galactose, aldonic acid, glucitose,

maltose, cellobiose, sucrose, trehalose, maltotriose, alginic acid and salts thereof, cyclodextrins, and celluloses.

[0031]

Examples of compounds which are compatible with water and which can improve the solubility of glycol ether having a low solubility in water and the ink ingredients and, in addition, can improve the penetration into recording media, for example, paper, or can be used for preventing clogging of the nozzles, include: alkyl alcohols having 1 to 4 carbon atoms; glycol ethers, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-propyl ether, diethylene glycol mono-iso-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-t-butyl ether, 1-methyl-1-methoxybutanol, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-iso-propyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-iso-propyl ether, propylene glycol mono-n-butyl ether, and dipropylene glycol mono-n-butyl ether; formamide; acetamide; dimethyl sulfoxide; sorbit; sorbitan; acetin; diacetin; triacetin; and sulfolane, and, from these compounds, suitable one can be selected and used.

[0032]

The ink according to the present invention may further comprise other surfactant from the viewpoint of regulating the

penetration of the ink, or regulating the surface tension of the ink. The surfactant is preferably highly compatible with the inks described in Examples. Further, the surfactant preferably has high penetration and is stable. Examples of the surfactants include amphoteric surfactants and nonionic surfactants. Specific examples of amphoteric surfactants include lauryldimethylaminoacetic acid betaine, 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine, coconut oil fatty acid amide propyldimethylaminoacetic acid betaine, polyoctylpolyaminoethylglycine, and imidazoline derivatives. Specific examples of nonionic surfactants include ether surfactants, such as polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene dodecylphenyl ether, polyoxyethylene alkylallyl ether, polyoxyethylene oleyl ether, polyoxyethylene lauryl ether, polyoxyethylene alkyl ether, and polyoxyalkylene alkyl ether, polyoxyethyleneoleic acid, ester surfactants, such as polyoxyethyleneoleic ester, polyoxyethylenedistearic ester, sorbitan laurate, sorbitan monostearate, sorbitan monooleate, sorbitan sesquioleate, polyoxyethylene monooleate, and polyoxyethylene stearate, and fluorosurfactants, such as fluoroalkyl esters and salts of perfluoroalkylcarboxylic acid.

[0033]

Further, for example, sodium benzoate, pentachlorophenol sodium, 2-pyridinethiol-1-oxide sodium, sodium sorbate, sodium dehydroacetate, and 1,2-dibenzothiazolin-3-one (Proxel CRL, Proxel BDN, Proxel GXL, Proxel XL-2, and Proxel TN, manufactured by ICI) may be added as preservatives and antimolds.

[0034]

Furthermore, pH adjustors, solubilizers, or antioxidants usable herein include: amines, for example,

alkanolamines, such as diethanolamine, triethanolamine, and propanolamine, alkylalkanolamines, such as methyldiethanolamine, dimethylethanolamine, ethyldiethanolamine, and diethylethanolamine, and morpholine, and modification products thereof; inorganic salts, such as potassium hydroxide, sodium hydroxide, and lithium hydroxide; ammonium hydroxide; quaternary ammonium hydroxide (such as tetramethylammonium); salts of carbonic acid, such as potassium carbonate, sodium carbonate, and lithium carbonate; salts of phosphoric acid; N-methyl-2-pyrrolidone; urea compounds, such as urea, thiourea, and tetramethylurea; allophanates, such as allophanate and methyl allophanate; biurets, such as biuret, dimethylbiuret, and tetramethylbiuret; and L-ascorbic acid and salts thereof.

[0035]

Furthermore, viscosity modifiers include rosins, alginic acids, polyvinyl alcohol, hydroxypropylcellulose, carboxymethylcellulose, hydroxyethylcellulose, methylcellulose, salts of polyacrylic acid, polyvinylpyrrolidone, gum arabic, and starch.

[0036]

Next, specific embodiments will be described.

[0037]

The water-soluble colorants are described in the cases where a dye are used, where a pigment is used, and where a dye and a pigment are used in combination.

[0038]

Water-soluble pigments 1 to 4 in the following description were prepared by oxidizing the surface of carbon black having a particle diameter of 10 to 300 nm to introduce dispersing groups, such as carbonyl, carboxyl, hydroxyl, or sulfone groups. In the following description, the average

particle diameters of the pigment particles are indicated on the basis of the unit of nm within parentheses after the pigment. Water-soluble dye 1 is Direct Black 154, water-soluble dye 2 is Direct Yellow 132, water-soluble dye 3 is Direct Blue 86, and water-soluble dye 4 is Acid Red 52.

[0039]

| Example 1 | Amount added (wt%) |
|---|---|
| Water-soluble pigment 1 (105) | 5.0 |
| Compound (1) of formula (I) | 8.0 |
| DEGmBE | 8.0 |
| OLFINE STG | 0.8 |
| Diethylene glycol | 10.0 |
| 2-Pyrrolidone | 5.0 |
| Triethanolamine | 0.8 |
| Ion-exchanged water | Balance |

In formula (I) representing compound (1), n is 2 and EP represents only ethyleneoxy.

[0040]

| Example 2 | |
|---|---|
| Water-soluble pigment 2 (85) | 4.5 |
| Compound (2) of formula (I) | 10.0 |
| DPGmBE | 3.0 |
| DEGmBE | 5.0 |
| OLFINE E 1010 | 1.0 |
| Dipropylene glycol | 5.0 |
| Surfynol 465 | 1.2 |
| Triethanolamine | 0.9 |
| Ion-exchanged water | Balance |

In formula (I) representing compound (2), n is 0.8 and EP represents only ethyleneoxy.

[0041]

Example 3

| | |
|---|---|
| Water-soluble pigment 3 (90) | 5.5 |
| Compound (3) of formula (I) | 2.0 |
| PGmBE | 3.5 |
| TEGmBE | 5.0 |
| Surfynol 104 | 0.3 |
| Diethylene glycol | 7.0 |
| Thiodiglycol | 3.5 |
| 1,6-Hexanediol | 5.0 |
| Diethylethanolamine | 1.0 |
| Potassium hydroxide | 0.1 |
| Ion-exchanged water | Balance |

The compound (3) of formula (I) is such that n is 4 and, at the same time, ethyleneoxy and propyleneoxy are present in a ratio of 3 : 1.

[0042]

Example 4

| | |
|---|---|
| Water-soluble pigment 4 (80) | 5.0 |
| Water-soluble dye 1 | 1.0 |
| Compound (4) of formula (I) | 8.0 |
| DEGmBE | 5.0 |
| TEGmBE | 5.0 |
| Diethylene glycol | 3.0 |
| 1,5-Pentanediol | 2.0 |
| Dimethyl-2-imidazolidinone | 2.0 |
| Sodium benzoate | 0.1 |
| Triethanolamine | 0.7 |
| Ion-exchanged water | Balance |

In formula (I) representing compound (4), n is 1.5 and EP represents only ethyleneoxy.

[0043]

Example 5

| | |
|---|---|
| Water-soluble pigment 1 (105) | 3.0 |
| Water-soluble dye 1 | 1.0 |
| Compound (5) of formula (I) | 10.0 |
| DEGmBE | 9.0 |
| OLFINE STG | 0.3 |
| Glycerin | 7.0 |
| Triethanolamine | 0.9 |
| Ion-exchanged water | Balance |

In formula (I) representing compound (5), n is 2.8 and EP represents only ethyleneoxy.

[0044]

Example 6

| | |
|---|---|
| Water-soluble dye 2 | 5.0 |
| Compound (6) of formula (I) | 6.0 |
| DPGmBE | 4.0 |
| DEGmBE | 8.0 |
| Glycerin | 10.0 |
| Thiodiglycol | 2.0 |
| 1,5-Pentanediol | 1.0 |
| Triethanolamine | 0.9 |
| Ion-exchanged water | Balance |

In formula (I) representing compound (6), n is 3.5 and EP represents only ethyleneoxy.

[0045]

Example 7

| | |
|---|---|
| Water-soluble dye 3 | 5.0 |
| Compound (7) of formula (I) | 10.0 |
| DEGmBE | 8.0 |
| Glycerin | 5.0 |
| Trimethylolpropane | 1.0 |
| Trimethylolethane | 1.0 |

| | |
|---|---|
| Surfynol 465 | 1.0 |
| Triethanolamine | 0.5 |
| KOH | 0.05 |
| Ion-exchanged water | Balance |

In formula (I) representing compound (7), n is 10 and EP represents only ethyleneoxy.

[0046]

Example 8

| | |
|---|---|
| Water-soluble dye 4 | 5.5 |
| Compound (8) of formula (I) | 6.0 |
| DEGmBE | 5.0 |
| Glycerin | 5.0 |
| Diethylene glycol | 5.0 |
| Tetrapropylene glycol | 5.0 |
| Triethanolamine | 0.9 |
| KOH | 0.1 |
| Ion-exchanged water | Balance |

In formula (I) representing compound (8), n is 4.5 and EP represents only ethyleneoxy.

[0047]

The compositions of the inks used in the comparative examples are described below. The pigments used in the comparative examples are prepared by dispersing carbon black particles with the aid of a styrene-acrylic acid random copolymer dispersant. The average particle diameter of the pigment particles is indicated in the parentheses on the basis of nm unit.

[0048]

Comparative Example 1

| | |
|---|---|
| Water-soluble Pigment 9 (90) | 5.0 |
| Glycerin | 10.0 |
| Dispersant | 3.0 |

| | |
|---|---|
| Nonionic surfactant | 1.0 |
| Ion-exchanged water | Balance |
| Comparative Example 2 | |
| Water-soluble dye (Food Black 2) | 5.5 |
| DEGmME | 7.0 |
| Diethylene glycol | 10.0 |
| 2-Pyrrolidone | 5.0 |
| Ion-exchanged water | Balance |
| Comparative Example 3 | |
| Water-soluble Pigment 11 (110) | 5.5 |
| Water-soluble dye (Food Black 2) | 2.5 |
| Diethylene glycol | 10.0 |
| Nonionic surfactant | 1.0 |
| Ion-exchanged water | Balance |

In the above description, DEGmBE represents diethylene glycol monobutyl ether, TEGmBE triethylene glycol monobutyl ether, PGmBE propylene glycol monobutyl ether, DPGmBE dipropylene glycol monobutyl ether, and DEGmME diethylene glycol monomethyl ether.

[0049]

For all the inks of Examples 1 to 8, the ejection stability was good, and Table 1 shows the ejection stability which was evaluated as to the inks wherein the amount of the colorant was reduced to half, and the difference in viscosity is regulated to fall within 5% by increasing the amount of the compound alone of formula(I) in each of Examples or the amount of glycerin and the ink wherein the difference in viscosity is regulated to fall within 5% by the addition of compounds other than glycerin. In Table 1, A represents "very good," B "good," C "bad," and D "very bad."

[0050]

[Table 1]

Results of evaluation test of ejection stability by viscosity modifiers

| | Examples | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Compound of formula (I) | A | A | A | A | A | A | A | A |
| Glycerin | A | B | A | A | A | A | A | A |
| Polyethylene glycol 1000 | D | C | D | D | B | C | B | C |
| Ethylene oxide (30 mol) adduct of glycerin | D | D | D | D | C | D | C | D |
| Polysaccharide (mixture of tetra- or higher straight-chain oligosaccharides) | D | D | D | D | C | D | C | D |

[0051]

The result of Table 1 apparently shows that the ink-jet recording ink according to the present invention provides good ejection stability. The inks having bad ejection stability are likely to have unstable frequency characteristics and separately requires individual mechanisms controlling the amount of the ejected ink. Further, the inks wherein, in the ink compositions of Examples 1 to 8, the colorant was replaced to regulate the viscosity within not more than 5% by using the compound of formula (I), similarly provide good ejection stability, and the frequency characteristics thereof are unlikely to be different. The ink set system for ink jet recording according to the present invention can realize the control of ink ejection through a single mechanism.

[0052]

The results of print quality evaluation are summarized in Table 2. In Table 2, A represents "very good," B "good," C "bad," and D "very bad."

[0053]

[Table 2]
Results of print quality evaluation test

| | Examples | | | | | | | | Comparative Examples | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 1 | 2 | 3 |
| Conqueror | A | A | A | A | A | A | A | A | C | C | C |
| Favorit | A | A | A | A | A | A | A | A | D | D | D |
| Modo Copy | A | A | A | A | A | A | A | A | C | D | D |
| Rapid Copy | A | A | A | A | A | A | A | A | C | D | D |
| EPSON KPP | A | A | A | A | A | A | A | A | C | C | D |
| Xerox P | A | A | A | A | A | A | A | A | B | D | D |
| Xerox 4024 | A | A | A | A | A | A | A | A | C | D | D |
| Xerox 10 | A | A | A | A | A | A | A | A | C | D | D |
| Neenha Bond | A | B | A | A | A | A | A | A | C | D | D |
| Ricopy 6200 | A | A | A | A | A | A | A | A | C | C | D |
| Yamayuri | A | B | A | A | A | A | A | A | D | D | D |
| Xerox R | A | A | A | A | A | A | A | A | C | D | D |

[0054]

The result of Table 2 apparently shows that the ink for ink jet recording system according to the present invention provides good print quality by the use of the compound of formula (I). Accordingly, the ink jet recording apparatus using the ink jet recording system according to the present invention has improved ejection stability and can realize prints having higher quality.

[0055]

Accordingly, in the present invention, the improvements of printing quality and clogging prevention are made by the use of the compound formula (I) which is an essential component, and, in the system using a plurality of inks, good ejection stability is provided by controlling the viscosity difference within 5% by the use of the compound of formula (I) or the combined use of the compound represented by formula (I) and glycerin, thereby obtaining the ink set for ink jet recording which is less likely to cause the difference in frequency

characteristics and which can realize the control of ink ejection through a single mechanism.

[0056]

These printing evaluation tests were conducted by means of an ink jet printer MJ-930C manufactured by Seiko Epson Corporation. In these evaluation tests, plain papers commercially available in Europe, America, and Japan, specifically Conqueror, Favorit, Modo Copy, Rapid Copy, EPSON EPP, Xerox 4024, Xerox 10, Neenha Bond, Ricopy 6200, Yamayuri, and Xerox R, were used as test papers.

[0057]

Further, in the balance water in Examples, 0.001 to 0.05% of benzotriazole was added for preventing the corrosion of ink jet recording head members, and 0.01 to 0.03% of EDTA was added for reducing the influence of metal ions contained in the ink system.

[0058]

The ink-jet recording ink according to the present invention is preferably used in a head wherein ink ejection responses to an electrostrictive element. A method wherein a head portion is heated disadvantageously involves a problem that the head is likely to clog since the colorants contained in ink and other ingredients are decomposed. The case where an electrostrictive element is used does not cause the problem, whereby the ink jet recording apparatus according to the present invention can be stably working. Further, the ink-jet recording ink according to the present invention, which comprises the compound of formula (I) and uses electrostrictive element, can improve clogging prevention. For example, the ink composition of Example 1 was loaded into an ink jet printer MJ-930C, and the printer was allowed to stand under conditions of temperature 60°C and relative humidity 40% for one week. One

week after the initiation of the standing, this printer required not more than three cleaning operations for return to normal ejection of the ink composition through all the nozzles. On the other hand, the same test was carried out for the ink compositions to which the compound represented by formula (I) had not been added. As a result, three or more cleaning operations were necessary for return to normal ejection. The printer MJ-930C is a printer wherein a head using a piezoelectric element, which is an electrostrictive element, has been adopted.

[0059]

As described above, the use of the compound of (I) is preferred from the viewpoint of the stability and actual use of an ink jet system. In the case of multi-color printing using an electrostrictive element in the present invention, however, when the difference in viscosity between the individual inks is varied to 5% or more, the frequency dependency on the ejected amount between each color inks become different, so that the dot size on a recording medium tends to vary. In an ink jet recording apparatus using light inks wherein the amount of the colorant is halved in Examples 1 to 8, an ink jet recording apparatus using a plurality of color inks, an ink jet recording apparatus using black and a plurality of color ink, or the like, when the viscosity difference increases to be 5% or more, the dot amount varies depending on the ejection frequency of the ink, so that it is necessary to separately provide mechanisms regulating ink ejection individually for inks. Accordingly, it is preferred to control the viscosity difference within 5% or less. In the present invention, such a viscosity control is easily made by the use of the compound of (I) or the combined use of the compound (I) and glycerin, compared with the use of other compounds. Further, this invention can make frequency

characteristics of ink ejection constant. In this case, the viscosity control is made by using another polyethylene glycol having a high molecular weight or polysaccharide, the frequency characteristics tend to vary. Accordingly, the viscosity control is preferably carried out by the use of the compound of (I) or the combined use of the compound (I) and glycerin.

[0060]

In ink using a relatively large amount of solid matter such as colorants as in the present invention, when the ink is not ejected for a long period of time, the ink dries on the front face of the nozzle in the recording head and thus is thickened, often leading to print disorder. By contrast, this problem can be overcome by delicately moving the ink at the front face of the nozzle on such a level that does not eject the ink from the nozzle, thereby stirring the ink, so that stable ink ejection can be carried out. The stable ink ejection can be easily controlled according to the head using an electrostrictive element. Such control cannot be made by a method wherein a portion very close to a nozzle is rapidly heated to create a bubble. Therefore, by employing this mechanism using an ink-jet recording ink according to the present invention, it is possible to increase colorant density in the ink and, when the colorant is a pigment and a material which is likely to create a bubble is used, it is also possible to increase color density and to offer stable ink ejection.

[0061]

Accordingly, the present invention provides an ink set for ink jet recording having an improved stable ink ejection particularly in the head using an electrostrictive element. The present invention can provide a significantly useful ink set for ink jet recording which reduces feathering or bleeding of printing images on recording media such as paper and, at the

same time, which is less likely to cause clogging even when used particularly in recording heads using an electrostrictive element.

[0062]

The present invention is not limited to Examples described here. Moreover, it is possible to make various modifications without departing from the framework of the invention.

[0063]

[ADVANTAGEOUS EFFECTS OF THE INVENTION]

As described above, the present invention provides an ink for use in an ink jet recording which can realize no bleeding prints on plain paper, particularly on recycled paper and also provides an advantage that the ink is less likely to cause a clogging problem particularly when used in a head using an electrostrictive element.

[TITLE OF DOCUMENT] ABSTRACT

[ABSTRACT]

[OBJECT OF THE INVENTION] To provide an ink set for use in an ink jet recording and an apparatus using the same which can offer improved stable ejection and, in the present invention, to provide a significantly useful ink-jet recording ink which reduces feathering or bleeding of printing images on recording media such as paper and, at the same time, which is less likely to cause a clogging problem even when used particularly in recording heads using an electrostrictive element.

[MEANS FOR ATTAINING THE OBJECT] In an ink-jet recording ink used for an ink jet recording apparatus using at least two or more inks, the difference in viscosity between the two or more inks at 15°C to 45°C is controlled to fall within 5% by the amount of a compound represented by the following formula (I) as a component of the ink-jet recording ink.

[Chemical formula 1]

formula (I):

$$G1\text{-}(EP)_n$$

wherein

G1 represents a glycerin structure;

EP represents an ethyleneoxy and/or propyleneoxy group, optionally, an OH group; and

n represents an average of addition units, ranging from 0.5 to 10.

[SELECTED FIGURE] None